

What is claimed is:

1. A radiation-curable formulation substantially-free of volatile organic compounds (VOCs), the formulation comprising

(a) from about 5% to about 70% by weight of a monomer diluent comprising at least one activated unsaturated moiety;

(b) optionally up to about 10% by weight a photo-initiator; and

(c) from about 30% to about 95% by weight of at least one polymer and/or oligomer obtained and/or obtainable from a monomer comprising at least one activated unsaturated moiety,

where the formulation and/or components thereof exhibit at least one of the following properties:

(w) the polymer component (c) has a solubility parameter (SP) of more than about $15 \text{ J}^{1/2} \text{ cm}^{-3/2}$;

(x) the polymeric component (c) has a number average molecular weight (M_n) of less than about 15,000 daltons;

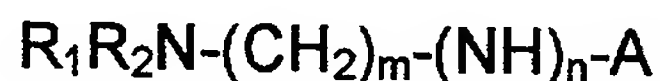
(y) the formulation has a viscosity of up to about 10,000 centipoise and no more than 50% of diluent; and/or

(z) the polymeric component (c) having a dispersing power (Θ) as defined herein of up to about 1.0 .

2. The formulation as claimed in claim 1, in which component (a) and component (c) are the same.

3. The formulation as claimed in claim 1 in which component (a) and component (c) comprise at least one:

semi-telechelic nitrogen-functional oligomers of formula



in which

A is a macromonomer moiety bearing at least one pendant ethylenic unsaturation with a degree of polymerization from about 2 to about 50;

n is 0 or 1;

m is from 0 to 18

R₁ and R₂ are both independently selected from H, and optionally substituted C₁₋₁₈hydrocarbo.

4. The formulation as claimed in claim 1 in which component (a) and component (c) comprise at least one:

low molecular weight vinylic polymers of at least one monoalkenyl aromatic monomer and at least one acrylic monomer having a dispersion index less than about 2 and a number average molecular weight from about 1000 to 6000 obtained and/or obtainable by a bulk polymerization process which comprises the steps of continuously:

(a) charging a mixture of vinylic monomers into a continuous stirred reactor zone containing a molten resin mixture of unreacted vinylic monomers and said vinylic polymer product;

(b) maintaining the molten resin mixture at a reaction temperature from about 235°C. to 310°C.; and

(c) maintaining a flow rate through said reaction zone sufficient (1) to provide a residence time of said charged vinylic monomer mixture in said reaction zone of at least about 2 minutes to provide a reaction product; and (2) to maintain a predetermined level of reaction mixture in said reaction zone.

5. The formulation as claimed in claim 1 in which component (a) and component (c) comprise at least one:

low molecular weight vinylic polymer having a narrow molecular weight distribution and optionally a low chromophore content, the polymer obtained

and/or obtainable by a bulk polymerization process comprising the steps of continuously:

(a) charging into a continuous mixed reactor zone containing a molten resin mixture;

(i) a mixture of vinyl monomers comprising at least one monoalkenyl aromatic monomer and at least one acrylic monomer;

(ii) a polymerization initiator in amounts to provide a molar ratio of said initiator to said mixture of vinyl monomers from about 0.0005:1 to 0.04:1;

(iii) from about 0 to 25 percent based on the weight of vinyl monomers of a reaction solvent, wherein said molten resin mixture comprises unreacted vinylic monomers and the vinylic polymer product;

(b) maintaining a flow rate through said reaction zone sufficient to:

(i) provide a residence time of said charged vinylic monomer mixture in said reaction zone of from about two minutes to one hour; and

(ii) maintain a predetermined level of reaction mixture in said reaction zone, and;

(c) maintaining the molten resin mixture at a reaction temperature within the range from about 180°C. to 270°C. sufficient to provide accelerated conversion to a readily processable, uniform, concentrated polymer product having a number average molecular weight of 500 to 6000, a polydispersity of less than about 2.5 and a distribution index of less than about 4.5

6. The formulation as claimed in claim 1 in which component (a) and component (c) comprise at least one:

high solids, non-styrenic acrylic polymers having a number average molecular weight of about 1000 to 2500 a polydispersity of less than about 3; a dispersion index of up to about 5 and optionally a low chromophore content, the polymer obtained and/or obtainable by a continuous bulk polymerization process comprising the steps of continuously:

(a) charging into a continuous mixed reactor zone containing a molten resin mixture consisting essentially of;

(i) at least one acrylic monomer;

(ii) a polymerization initiator in amounts to provide a molar ratio of said initiator to said acrylic monomer from about 0.0005:1 to 0.06:1,

(iii) from about 0 to 25 percent based on the weight of acrylic monomers of a reaction solvent, wherein said molten resin mixture comprises unreacted acrylic monomers and the acrylic polymer product;

(b) maintaining a flow rate through said reaction zone sufficient to:

(i) provide a residence time of said charged acrylic monomer in said reaction zone of from about 1-30 minutes; and

(ii) maintain a predetermined level of reaction mixture in said reaction zone, and;

(c) maintaining the molten resin mixture at a reaction temperature within the range of from about 180°C. to 270°C. sufficient to provide a uniform, concentrated polymer product optionally at an accelerated conversion and optionally such that the product is readily processable, wherein the product has a number average molecular weight of 500 to 6000, a polydispersity of less than about 2.5 and a distribution index of less than about 4.5

7. The formulation as claimed in claim 1 in which component (a) and component (c) comprise at least one:

low molecular weight hydroxy-functional acrylate resins optionally water reducible and/or water dispersible, the resin comprising recurring units of:

(a) an allylic alcohol optionally in amount of about 5 to about 50% by weight, the alcohol having the general structure:



in which

n is less than about 3.0;

A is a (C₁₋₁₂hydrocarbylene)oxy group; and

R is selected from the group consisting of: hydrogen and C₁₋₁₂hydrocarbyl;
 (b) a C₁₋₂₀hydrocarbyl; vinyl aromatic; aryl acrylate and/or methacrylate monomer; optionally in amount of about 50% to about 90% by weight;
 (c) optionally, one or more ethylenically unsaturated monomers (optionally in an amount from about 1 to about 50% by weight), the monomers selected from the group consisting of vinyl aromatic monomers, unsaturated nitriles, vinyl esters, vinyl ethers, vinyl halides, vinylidene halides, unsaturated anhydrides, unsaturated dicarboxylic acids, (meth)acrylic acids; (meth)acrylates, (meth)acrylamides and conjugated dienes;

where the acrylate resin has:

a hydroxyl number from about 15 to about 500 mg KOH/g;
 an acid number within the range of about 5 to about 330 mg KOH/g;
 a number average molecular weight M_n from about 500 to about 10,000 daltons;
 and/or
 a T_g from about -20°C. to about 50°C as measured by differential scanning calorimetry (DSC).

8. The formulation as claimed in claim 1 in which component (a) and component (c) comprise at least one:

low-molecular-weight, hydroxy-functional acrylate resins which comprise recurring units of:

(a) a propoxylated allylic alcohol of the formula



in which

A is an oxypropylene group,

R is selected from the group consisting of hydrogen and C₁₋₅alkyl, and

n, which is the average number of oxypropylene groups in the propoxylated allylic alcohol, has a value less than or equal to 2;

(b) C₁₋₂₀alkyl or aryl acrylate or methacrylate monomer, and

(c) optionally, one or more ethylenic monomers selected from the group consisting of vinyl aromatic monomers, unsaturated nitriles, vinyl esters, vinyl ethers, vinyl halides, vinylidene halides, unsaturated anhydrides, unsaturated dicarboxylic acids, (meth)acrylic acids, (meth)acrylamides and conjugated dienes;

where the acrylate resin has a hydroxyl number within the range of about 50 to about 450 mg KOH/g, and a number average molecular weight within the range of about 500 to about 10,000.

9. The formulation as claimed in claim 1 in which component (a) and component (c) comprise at least one:

low molecular weight, hydroxy functional acrylate resins which comprise recurring units of:

(a) an allylic alcohol having the general structure



in which R is selected from the group consisting of hydrogen and C₁₋₅alkyl, and

(b) a C₁₋₂₀alkyl or aryl acrylate or methacrylate monomer; and

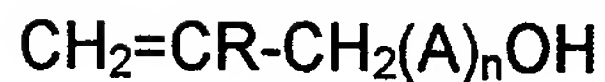
(c) optionally, one or more ethylenic monomers selected from the group consisting of vinyl aromatic monomers, unsaturated nitriles, vinyl esters, vinyl ethers, vinyl halides, vinylidene halides, unsaturated anhydrides, unsaturated dicarboxylic acids, acrylic and methacrylic acids, acrylamide and methacrylamide, and conjugated dienes;

wherein the acrylate resin has a hydroxyl number within the range of about 20 to about 500 mg KOH/g, and a number average molecular weight within the range of about 500 to about 10,000.

10. The formulation as claimed in claim 1 in which component (a) and component (c) comprise at least one:

acrylic resins which comprise recurring units of:

(1) an allylic alcohol or a propoxylated allyl alcohol of the formula



in which

A is an oxypropylene group,

R is selected from the group consisting of hydrogen and C₁₋₅alkyl, and

n, which is the average number of oxypropylene groups in the propoxylated allylic alcohol has a value within the range of about 1 to about 2;

(2) a vinyl aromatic monomer; and

(3) one or more C₁₋₂₀alkyl or aryl acrylate or methacrylate monomers;

where the resin has a glass-transition temperature within the range of about – 20°C. to about 50°C., a hydroxyl number within the range of about 60 to about 160 mg KOH/g, and a number average molecular weight within the range of about 1000 to about 5000

11. The formulation as claimed in claim 1 in which component (a) and component (c) comprise at least one:

water reducible and/or water dispersible resins which comprise recurring units of:

(1) from about 5 to about 50% by weight of an allylic alcohol or a propoxylated allyl alcohol of the formula



in which

A is an oxypropylene group,

R is selected from the group consisting of hydrogen and C₁₋₅alkyl, and

n, which is the average number of oxypropylene groups in the propoxylated allylic alcohol has a value within the range of about 1 to about 2;

(2) from about 50 to about 90% by weight of a vinyl aromatic monomer; and

(3) from about 1 to about 50% by weight of an acrylic acid monomer;

where the resin has a number average molecular weight within the range of about 500 to about 10,000, a hydroxyl number within the range of about 15 to

about 250 mg KOH/g, and an acid number within the range of about 5 to about 330 mg KOH/g.

12. The formulation as claimed in claim 1, where component (c) has a SP of from about $15 \text{ J}^{1/2}\text{cm}^{-3/2}$ to about $30 \text{ J}^{1/2}\text{cm}^{-3/2}$.

13. The formulation as claimed in claim 12, where component (c) has a SP from about $18 \text{ J}^{1/2}\text{cm}^{-3/2}$ to about $25 \text{ J}^{1/2}\text{cm}^{-3/2}$.

14. The formulation as claimed in claim 1, where component (c) has a number average molecular weight (M_n) from about 200 to about 20,000 daltons.

15. The formulation as claimed in claim 14, where component (c) has a number average molecular weight (M_n) from about 500 to about 15,000 daltons.

16. The formulation as claimed in claim 1, where component (c) has a number average molecular weight (M_n) from about 1,000 to about 10,000 daltons.

17. The formulation as claimed in claim 1, with a viscosity of up to about 2,000 centipoise per g of polymeric component (c) at a temperature of 25°C.

18. The formulation as claimed in claim 1, where the polymeric component (c) has a dispersing power (Θ) from about 1×10^{-5} to about 0.8 DP(equivalents) / (mol x daltons).

19. The formulation as claimed in claim 18, where the polymeric component (c) has a Θ from about 1×10^{-3} to about 0.5 DP(equivalents) / (mol x daltons).

20. The formulation as claimed in claim 19, where the polymeric component (c) has a Θ from about 0.01 to about 0.1 DP(equivalents) / (mol x daltons).

21. The formulation as claimed in claim 1 claim which further comprises a pigment.

22. The formulation as claimed in claim 21, which is an ink effective for use in flexography, and/or lithography.

23. A flexographic or lithographic method which employs the formulation as claimed in claim 1.

24. An article printed by a formulation as claimed in claim 1.

25. A process for printing an article comprising the steps of:

- (a) applying thereto a formulation as claimed in claim 1;
- (b) irradiating said article sufficiently to cause polymerization of the formulation thereon.